Thermochimica Acta 492 (2009) 67–72

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Critical rate of cooling for suppression of crystallization in random copolymers of propylene with ethylene and 1-butene

D. Mileva[a], R. Androsch[a,*], E. Zhuravlev[b], C. Schick[b]

[a] Martin-Luther-University Halle-Wittenberg, Center of Engineering Sciences, D-06099 Halle/Saale, Germany
[b] University of Rostock, Institute of Physics, D-18051 Rostock, Germany

ARTICLE INFO

Article history:
Available online 5 April 2009

Keywords:
Propylene–ethylene and propylene–1-butene random copolymer
Crystallization
Crystal reorganization
Fast scanning nanocalorimetry

ABSTRACT

Fast scanning calorimetry has been employed for evaluation of the critical rate of cooling for complete suppression of non-isothermal melt-crystallization of random copolymers of propylene with low amount of ethylene or 1-butene. While crystallization/mesophase formation of isotactic polypropylene can only be suppressed by cooling the quiescent melt at rates faster than 300 K s^{-1}, in case of random copolymers the critical cooling rate for complete inhibition of crystallization is shifted to lower rate as a function of the concentration of co-units. Preparations with about 10 mol% ethylene or 1-butene do not crystallize if the cooling rate exceeds 100 K s^{-1}. Subsequent cold-crystallization and reorganization of mesomorphic structure, formed by aging of initially fully amorphous samples at ambient temperature, can only be avoided by heating with a rate faster than 5000 K s^{-1}. Fast heating of quenched and at ambient temperature aged specimens, which only contained mesomorphic domains in an amorphous matrix, revealed that the melting temperature of mesomorphic structure is about 350 K.

1. Introduction

It is known since the first synthesis of isotactic polypropylene (iPP) in the middle of the last century that crystallization of the quiescent melt of iPP at low cooling rate, or at low supercooling, respectively, results in formation of monoclinic α-crystals, while fast cooling/quenching leads to formation of a less stable mesophase [1,2]. This observation was quantified about 40 years later regarding the exact rate of cooling at which formation of monoclinic crystals is replaced by formation of mesomorphic domains [3]. In a special device [4], films of iPP were quenched in cold water in contact with a thermocouple for recording the temperature–time profile during rapid cooling. Subsequently these films were analyzed regarding their X-ray structure and macroscopic density. These analyses provided the information that mesophase formation in iPP occurs if the melt is cooled at a rate of about 50–100 K s^{-1}, or faster. Generation of fully amorphous specimens was not possible since quenched samples crystallized ultimately at the temperature of the coolant, which was distinctly higher than the glass transition temperature of fully amorphous iPP [3,5]. It has been shown that quenching to a temperature lower than the glass transition temperature of fully amorphous iPP of about 250–260 K even inhibited formation of the mesophase, which, however, immediately developed on subsequent heating to temperatures higher than the glass transition [6–8].

Further progress in characterization of the crystallization behavior of iPP on rapid cooling, or on isothermal crystallization at low temperature was achieved by application of recently introduced fast scanning nanocalorimetry (FSC) [9–11]. This technique allowed the measurement of the temperature of crystallization of iPP on controlled rapid cooling, and confirmed that the critical rate of cooling for mesophase formation in iPP is about 100 K s^{-1} [12,13]. Cooling at low rate between 0.1 and 160 K s^{-1} led to the development of monoclinic crystals at crystallization temperatures between about 115 and 75 °C, respectively. Mesophase formation, in contrast, occurred on cooling at rates between 80 and 300 K s^{-1} at much lower temperature between 40 and 20 °C. Furthermore, it was found that even mesophase formation can be suppressed by cooling at rates higher than 1000 K s^{-1}, preserving a fully amorphous state of specimens at low temperatures.

Recently, FSC has been employed to evaluate rates of isothermal crystallization as a function of temperature in a wide range between 0 and 110 °C [14,15]. The observed dependence of the time of crystallization on the temperature of crystallization showed two distinct minima at about 20–30 °C and 80–90 °C, which were related to the maximum rate of crystallization of mesophase and of monoclinic crystals, respectively, confirming the earlier, non-isothermal FSC investigations.

In the present study it is intended to evaluate the effect of random incorporation of low amount of either ethylene or 1-butene

---

[*] Corresponding author. Tel.: +49 3461 463762; fax: +49 3461 463891.
E-mail address: rene.androsch@iw.uni-halle.de (R. Androsch).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.03.019

into the iPP macromolecule on the crystallization behavior at rapid cooling. It is an extension of our previous research about the structure and structure–property relations of the iPP homopolymer [16–19] and random copolymers of iPP with 1-alkenes [20,21], which included in particular the evaluation of the morphology and thermodynamic stability of monoclinic crystals and mesomorphic domains as a function of the condition of primary crystallization and subsequent annealing. Analysis of the crystallization of random propylene–ethylene (iPP–Eth) and propylene–1-butene copolymers (iPP–But) showed that the crystallinity, the crystal size and the temperature of crystallization were lower than in iPP crystallized at identical cooling conditions [20–24]. Though the change of kinetics of crystallization and of the super-molecular structure in iPP random copolymers is on purpose, since it opens new fields of commercial applications [25], there is still lack of knowledge about the crystallization at rapid cooling. There exist only a few studies which showed that rapid cooling of iPP–Eth and iPP–But random copolymers leads to development of mesomorphic, non-lamellar domains similar as in the iPP homopolymer, with the exact condition of formation, that is, supercooling/temperature of crystallization, however, not yet specified [20,21,26–28]. Experiments for quantitative evaluation of the critical rate of cooling for observation of fully amorphous iPP–Eth and iPP–But random copolymers were not performed to date, and are therefore the primary subject of the present investigation. In addition, we used the capability of fast scanning calorimetry to analyze the melting and reorganization behaviors of initially fully amorphous and at ambient temperature aged samples.

2. Experimental

2.1. Materials

Random Ziegler–Natta catalyzed isotactic propylene–ethylene copolymers (iPP–Eth) with ethylene contents of 3.4 and 8 mol% were provided by Borealis (Austria). The molar mass and the polydispersity of these samples were about 400,000 g mol^{-1} and 3.8, respectively [29]. Isotactic propylene–1-butene copolymers (iPP–But) with 1-butene concentrations of 6.0 and 10.9 mol% were purchased from Sigma–Aldrich. The mass-average molar mass and the polydispersity of these copolymers are 225,000 g mol^{-1} and 3.1, respectively. The iPP–Eth and iPP–But copolymers were provided in form of pellets, which were reshaped into films of 100 μm thickness by compression-molding, using a Perkin-Elmer laboratory press, operated in combination with a Lot-Oriel heating device/die.

2.2. Instrumentation

FSC was performed using a thin film chip sensor XI-321 of Xensor Integration (Netherlands) with a detailed description of the measurement principle and instrumental setup given elsewhere [9–11,30,31]. As an advance to earlier versions of the instrument, a differential configuration of two identical sensors has been used, for minimization of instrumental effects on the measured heat-flow rate. The use of the FSC calorimeter in a liquid nitrogen environment allows linear cooling of samples down to 100 K, which is of particular importance for analysis of the crystallization behavior of polypropylene and related random copolymers, since the glass transition occurs at sub-ambient temperature. From the compression-molded films, a small piece was cut and placed on the heated area of the sensor, with the thermal contact improved by Apiezon N$^{\mathrm{TM}}$ grease. Scanning was performed using rates of temperature change between 30 and 5000 K s^{-1}, on both heating and cooling. The samples were heated to 453 K, held at this temperature for 0.1 s and then cooled to 100 K, if not stated otherwise. The measurements were carried out under nitrogen atmosphere. The temperature signal of the thermopile of the sensor was calibrated by the melting temperatures of indium and lead, measured at different rate of heating. Correction of the thermal lag in cooling experiments was done using an identical calibration function as was used for correction of the thermal lag on heating. The mass of samples was of the order of nanograms, which was determined by normalization of the measured total heat capacity of a fully liquid sample with the specific heat capacity listed in the ATHAS data base [32].

Standard differential scanning calorimetry (DSC) data were collected using either a Pyris Diamond DSC or a DSC 7, both from Perkin-Elmer. The instruments were operated in conjunction with the cryogenic cooling accessory, using liquid nitrogen as coolant. The sample and reference furnaces were purged with gaseous nitrogen at a flow rate of 40 mL min^{-1}. The temperature and heat-flow rate were calibrated by evaluation of the onset temperatures of melting and the heat of fusion of metal standards, analyzed at 10 K min^{-1}. In case of the Pyris DSC, samples with a mass of about 1 mg were wrapped in aluminum foil, in order to minimize the thermal lag between sensor and sample, and scanned at rates of temperature change of 1, 4, and 6 K s^{-1} on cooling. The DSC 7 was employed to record crystallization and melting at low rate of temperature change of 0.16 or 0.3 K s^{-1}, respectively, using standard aluminum pans for encapsulation of samples.

3. Results and discussion

3.1. Primary crystallization

Fig. 1 shows as a typical example the apparent heat capacity of a random copolymer of propylene with 11 mol% 1-butene as a function temperature, obtained on cooling at different rate. The data serve for illustration of the effect of the rate of cooling on the temperature of maximum rate of crystallization, that is, on the crystallization peak temperature. The top curve was obtained on cooling at 0.16 K s^{-1}, or 10 K min^{-1}, respectively, which is typical in standard DSC experiments. The crystallization peak, recorded at this particular rate of cooling, is located at about 365 K, and decreases as expected with increasing rate of cooling. If cooling is performed at a rate of 50 K s^{-1}, using FSC, then the crystallization peak is observed

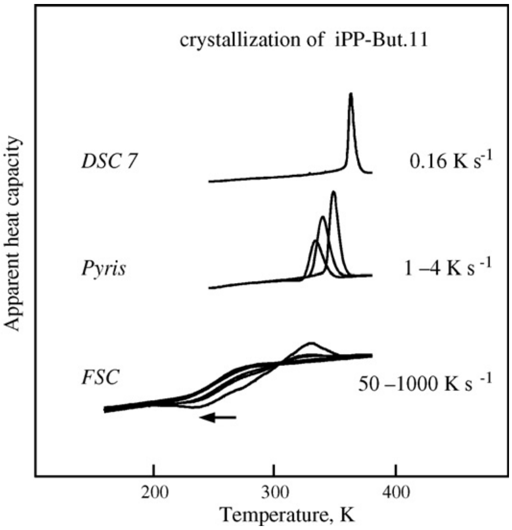

Fig. 1. Apparent heat capacity of a random propylene–1-butene copolymer with 11 mol% 1-butene as a function of temperature. Data were collected on cooling at different rate between 0.16 and 5000 K s^{-1}, using standard DSC and FSC, as is indicated in the plot.

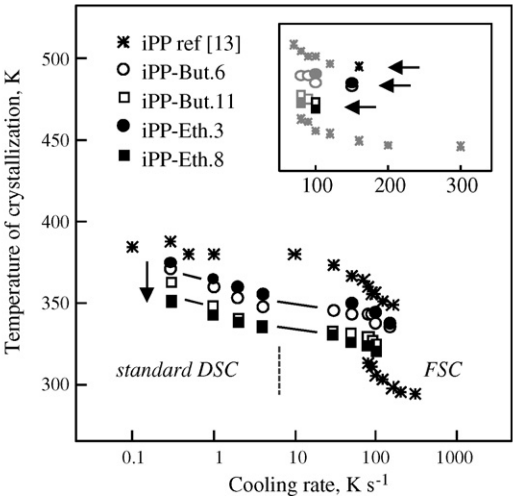

Fig. 2. Temperature of crystallization of isotactic polypropylene (asterisks), propylene–ethylene (filled symbols) and propylene–1-butene random copolymers (open symbols) as a function of cooling rate on melt-crystallization. The inset is an enlargement, showing data obtained on cooling between 100 and 300 K s^{-1} at an expanded scale.

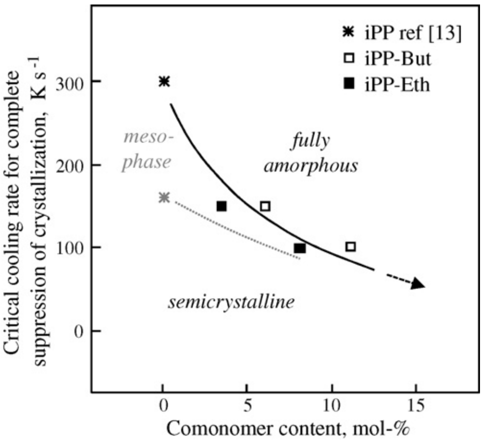

Fig. 3. Critical rate of cooling for complete suppression of crystallization of isotactic polypropylene as a function of the concentration of ethylene or 1-butene co-units. The black solid line indicates complete suppression of crystallization, and the gray dotted line indicates replacement of crystals by mesophase on increasing the rate of cooling.

at a temperature of only 330 K. Crystallization eventually is completely suppressed on cooling with a rate larger than 100 K s^{-1}, which is recognized by absence of any crystallization peak. Instead, a distinct step at the glass transition temperature is observed in the FSC curve. The glass transition temperature shifts to lower temperature if crystallization is completely suppressed, as is indicated with the horizontal arrow. This observation points to immobilization of the amorphous phase in presence of crystals, as has recently been investigated in detail on example of the iPP homopolymer [19].

Similar cooling experiments as are shown in Fig. 1 have been performed on all copolymers of the present study and are summarized in Fig. 2. It shows the temperature of crystallization as a function of the logarithm of the cooling rate, with the peak temperature defined as crystallization temperature. We selected the peak temperature for comparison of the effect of cooling rate on the crystallization instead of the onset temperature, in order to be consistent with earlier work in this field [13]. The open and filled symbols represent data obtained on iPP–But and iPP–Eth copolymers, respectively, and the asterisks represent data which were collected on an iPP homopolymer in a former study [13]. The vertical dotted line separates data points measured by standard DSC at low cooling rate, and data points measured by FSC at high cooling rate. First of all, it can be recognized that addition of ethylene and 1-butene comonomers both cause a decrease of the crystallization temperature in comparison to that of the iPP homopolymer. This is indicated with the vertical arrow, and is expected from former studies of the crystallization behavior of random iPP–1-alkene copolymers [22–24]. A major reason for the decrease of the crystallization temperature is the thermodynamically driven process of exclusion of co-units from crystallization, though thermodynamic equilibrium may not fully be achieved. While crystallization of random iPP–1-alkene copolymers at isothermal condition or on slow cooling has frequently been analyzed in the literature, the advance of the data of Fig. 2 is the evaluation of the crystallization behavior at rapid cooling. It is observed for all copolymers of the present study that an increase of the rate of cooling causes a decrease of the crystallization temperature. The decrease of the crystallization temperature of the copolymers is almost linear if the data are plotted as a function of the logarithm of the cooling rate, which is in accord with an earlier investigation, performed on short-chain branched polyethylene [33]. Crystallization of the iPP homopolymer at rates lower about 200 K s^{-1} leads to formation of monoclinic crystals at relatively high temperature, however, is peculiar from point-of-view that at fast cooling at rates larger than about 80 K s^{-1} there is observed a second, low temperature crystallization peak which was connected to formation of mesomorphic structure [13,16]. The formation of mesophase is then only suppressed on cooling faster than 300 K s^{-1}. In case of the copolymers of the present study, throughout, only a single crystallization event is detected, which does not allow a straightforward recognition of formation of different polymorphs as in case of the homopolymer. While analysis of the effect of the rate of cooling on generation of different polymorphs is subject of a companion study, since it requires availability of larger samples for X-ray investigations, focus of the present work is the evaluation of the critical cooling rate for complete suppression of crystallization. The data of Fig. 2 show clearly that copolymerization of propylene with both ethylene or 1-butene leads to a distinct reduction of the critical cooling rate for suppression of crystallization. Formation of monoclinic crystals and of mesophase is suppressed in the iPP homopolymer by cooling faster than 160 and 300 K s^{-1}, respectively, whereas in the investigated copolymers crystallization is absent on cooling at lower rate, depending on the concentration of co-units. For easy recognition of the effect of ethylene and 1-butene co-units on the critical rate of cooling for suppression of crystallization, temperatures of crystallization are shown on an expanded scale of the cooling rate in the inset of Fig. 2. The horizontal arrows indicate the points of interest in the present study, demonstrating the shift of last trace of crystallization to lower cooling rate on increasing concentration of co-units.

Fig. 3 is a plot of the critical rate of cooling for complete suppression of crystallization as a function of the concentration of ethylene or 1-butene co-units in the iPP chain. The critical rate of cooling for complete suppression of crystallization is defined as the maximum cooling rate at which crystallization still is observed, as is detected by an exothermic event/peak in the FSC experiment. The inset of Fig. 2 shows that in case of iPP the maximum rate of cooling for observation of crystallization is 300 K s^{-1}. This data point is then transferred to Fig. 3, and plotted at zero concentration of co-units. Similar, the maximum rate of cooling for observation of crystallization in the random iPP–Eth and iPP–But copolymers is re-drawn in Fig. 3, to address the effect of the concentration of ethylene and 1-butene co-units on the crystallization at rapid cooling. As was already concluded from the experimental raw data, the critical rate of cooling for complete suppression of crystallization decreases with increasing concentration of co-units. Note that we do not attempt to identify an effect of the type of co-units at the present stage of research. Such an evaluation would require identical chemical characteristics regarding branching or homogeneity of the comonomer distribution, respectively, which is not fulfilled in the present study. Therefore we have drawn only a single curve for guidance of the eye and easy reading of the condition for observation of a fully amorphous material. Cooling at a rate which is higher than is indicated by the black solid line yields a fully amorphous polymer, and cooling at lower rate, correspondingly, yields a semicrystalline polymer, containing either mesomorphic domains or monoclinic crystals in the iPP homopolymer, or a mixture of monoclinic and orthorhombic crystals in the copolymers. The data of Fig. 3 are in agreement with quantitative studies about the kinetics of crystallization in random copolymers of propylene with ethylene and 1-butene. It has been observed, that incorporation of co-units into the iPP chain is not only connected with a reduction of the temperature of crystallization, which finally is a consequence of a lowered equilibrium melting point [20,34–36], rather, in addition, causes a reduction of the maximum rate of crystallization [37]. We assume that it is the latter, which leads to the observed dependence of the critical rate of cooling as a function of concentration of co-units. Furthermore, the measured lowering of the critical rate of cooling for complete suppression of crystallization on addition of co-units into the iPP chain in the present study is in qualitative agreement with the experimental finding of a decrease of the thickness of lamellae on increasing comonomer concentration [20]. Both observations point to increasing hindrance of crystallization due to presence of co-units.

The arrow which extends the black solid line is intended to indicate that the critical rate of cooling may approach zero at large concentration of co-units in the iPP chain. In other words, crystallization may then not be suppressed by non-favorable condition of crystallization rather than by the large number of constitutional defects exceeding a critical concentration above which a filtering of crystallizable sequences does not allow formation of crystals of a minimum size. Alternatively, at large concentration of co-units in a copolymer, formation of different crystal structures may be triggered, allowing incorporation of co-units at larger concentration. Naturally that in the latter case the kinetics of crystallization qualitatively is changed, impossible to consider in the discussion of Fig. 3.

For the iPP homopolymer it is known that the formation of monoclinic crystals is completely replaced by formation of mesomorphic domains if the cooling rate exceeds 160 K s^{-1}. Correspondingly, we inserted at this cooling rate an additional data point in Fig. 3. In case of the copolymers, we were not detecting two discrete crystallization events which would point to such a qualitative change of the crystallization behavior. Based on prior X-ray investigations [20] we know, however, that mesophase formation also occurred in the copolymers of the present study when specimens were quenched from the liquid state and subsequently annealed at ambient temperature. We assume that due to the lowering of the crystallization temperature in the copolymers the critical rate of cooling for replacement of crystals by mesophase, and for full suppression of mesophase and crystal formation are closer than in the homopolymer. Crystal formation and mesophase formation may in the investigated copolymers therefore be superimposed and non-resolvable in the FSC experiment. Further X-ray studies are in progress, and confirm a replacement of monoclinic and orthorhombic crystals by mesomorphic domains in the analyzed copolymers, supporting our present view. For accommodation of this observation we inserted in Fig. 3 an additional, hypothetical line indicating the replacement of crystals by mesophase on increasing cooling rate. Again, this observation is qualitatively evidenced, however, not yet quantified with respect to the exact cooling rate.

Finally, it is important to stress that the data of Fig. 3 and their interpretation only are true if cooling at the specific rate is continued to a temperature below the glass transition. If cooling stops at a temperature higher than the glass transition temperature, mesophase or crystal formation immediately will start, invalidating the above statements. The related phenomenon of cold-crystallization and reorganization of a supercooled liquid is discussed further in the next section.

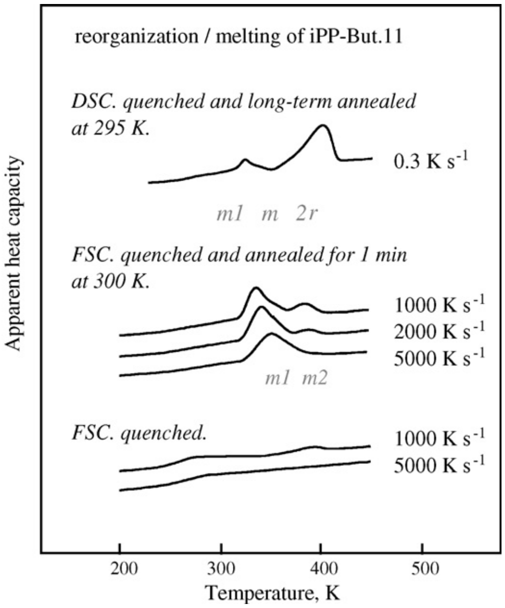

Fig. 4. Apparent heat capacity of a random propylene–1-butene copolymer with 11 mol% 1-butene as a function of temperature. Data were collected on heating at the specified rates, using standard DSC and FSC, as is indicated in the plot. The plot contains analyses of specimens of different thermal history, in order to qualitatively describe the reorganization behavior of initially fully amorphous preparations.

3.2. Cold-crystallization and reorganization

Fig. 4 shows the apparent heat capacity of random propylene–1-butene copolymers with a concentration of 1-butene of 11 mol% as a function of temperature. Specimens were crystallized as indicated in the legends and heated at different rate, in order to further evaluate the complex and not yet completely understood reorganization behavior of fully amorphous or amorphous–mesomorphic polypropylenes. Note that the data obtained on the particular random iPP–But copolymer with 11 mol% 1-butene are representative also for the copolymer with 6 mol% 1-butene. The top curve was obtained on a preparation which was quenched from the liquid state and subsequently aged at room temperature until a stationary structural state was achieved. The data were collected by standard DSC using a heating rate of 0.3 K s^{-1} (18 K min^{-1}) and reveal a weak glass transition at about 270 K, which is followed by a small endothermic peak at about 325 K (*m1*), a broad exothermic reorganization (*r*), and the final melting peak (*m2*). The enthalpy-based crystallinity of such a specimen is of the order of 30–40%. Interpretation of the DSC heating scan is not straightforward, since the endothermic peak at about 325 K (*m1*) indicates melting of mesomorphic domains, which immediately recrystallize as discussed in more detail in Ref. [38–41]. Obviously, the onset of melting of these mesomorphic domains immediately triggers large-scale reorganization, being connected with exothermic heat flow, and melting of reorganized crystals at higher temperature. The total effect seen in the calorimetric curves is close to zero because endothermic heat flow due to melting and exothermic heat flow due to recrystallization almost cancel out each other. Note that reorganization in this context covers: (a) the mesomorphic–monoclinic phase transition, (b) changes of the morphology of existing domains, and (c) classical cold-crystallization of the supercooled liquid. Despite this explanation of the heating scan of quenched and at ambient temperature annealed polypropylene sounds justified, based on the general knowledge of the metastability, and reorganization behavior of polymer crystals [42,43], there was not yet observed evidence that the low temperature melting peak between 320 and 330 K (*m1*) can be considered as temperature of melting of mesomorphic domains. Frequently it is interpreted as a classical annealing peak which would then only represent the thermodynamic stability of a fraction and not of the total population of mesomorphic domains [44,45]. We used therefore FSC to further evaluate the nature of the low temperature endothermic peak. The specimens which are represented with the center three curves in Fig. 4 were quenched to 100 K, subsequently heated to 300 K, cold-crystallized for a period of 1 min, and re-cooled to 100 K, with the heating and aging steps included for reproducible formation of mesophase. Subsequent melting was performed at rates of 1000, 2000, and 5000 K s^{-1}. Despite the time of annealing at room temperature of samples employed for FSC analyses (center three curves) is considerably shorter in comparison to that of the sample analyzed by standard DSC (top curve), we believe that the effect of different time of cold-crystallization on the amount and structure of formed mesophase is negligible in terms of a qualitative comparison of the reorganization behavior.

First of all, the comparison of the FSC experiments with the standard DSC experiment reveals a higher enthalpy of transition of the low temperature melting peak (*m1*), absence of exothermic reorganization (*r*), and a distinctly lower enthalpy of transition of the high temperature melting peak (*m2*) in the FSC experiments. The variation of the heating rate in the FSC experiment strengthens the observed trends. The enthalpy of transition of the peak (*m1*) increases and the enthalpy of transition of the melting peak (*m2*) decreases with increasing heating rate. From these observations we conclude that the low temperature melting peak (*m1*) must be considered as the temperature of melting of mesomorphic domains. The FSC data prove almost complete suppression of reorganization (*r*) of mesomorphic structure on fast heating, and a distinct reduction of the enthalpy of fusion of the high temperature melting peak (*m2*). In other words, complete suppression of relatively slow reorganization processes by fast heating with a rate of about 5000 K s^{-1}, or faster, leads to completion of melting of the mesomorphic domains at their inherent melting temperature, being lower about 350 K. Note that the degree of suppression of reorganization can easily be read from the enthalpy of melting at high temperature. The peak *m2* is absent only on heating at 5000 K s^{-1}, while heating at 1000 and 2000 K s^{-1} still allowed minor reorganization, as is indicated by non-zero melting *m2*. The small increase of the temperature of the first peak (*m1*) is due to superheating of the melting transition [46].

The two curves at the bottom of Fig. 4 confirm the conclusion of complete absence of reorganization on heating with a rate of 5000 K s^{-1}, or faster. The lower of the two curves was measured on a fully amorphous specimen with a rate of 5000 K s^{-1}. It shows the glass transition at sub-ambient temperature and then no further transition which would indicate crystallization, reorganization, or melting. In contrast, if the heating rate is lowered to 1000 K s^{-1}, then cold-crystallization is indicated by the shallow exothermic peak, followed by melting.

4. Summary

FSC has successfully been employed to further evaluate the crystallization behavior of random propylene–ethylene and propylene–1-butene copolymers at conditions which cannot be accessed by application of standard DSC. In particular it allowed the observation of critical rates of temperature change for complete inhibition of (a) melt-crystallization on cooling, (b) cold-crystallization of fully amorphous structure on heating, and (c) reorganization of mesomorphic structure, formed via cold-crystallization, on heating. While melt-crystallization gets completely suppressed on cooling at rates of magnitude of order of 10^2 K s^{-1}, inhibition of both cold-crystallization and reorganization on heating requires at least a rate of temperature change of 5000 K s^{-1}. Furthermore, it has been found that the critical rate of cooling for inhibition of melt-crystallization decreases with increasing concentration of co-units in copolymers. This result is consistent with the observation of a lowering of the temperature of crystallization and of the maximum rate of crystallization with increasing comonomer concentration, reported in the literature. Finally, FSC heating experiments on quenched and at ambient temperature aged specimens allowed determination of the melting temperature of mesomorphic polypropylene of about 340–350 K, which corresponds to the first melting peak in the DSC curves, often called “annealing peak”.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is greatly acknowledged. Daniela Mileva and René Androsch thank for kind assistance in experimentation by all members of the Polymer Physics group of Prof. Christoph Schick at the University of Rostock. Propylene–ethylene copolymers were kindly provided by Borealis Polyolefine GmbH (Austria).

References

[1] G. Natta, P. Corradini, Nuovo Cimento Suppl. 15 (1960) 5–40.
[2] G. Natta, Makromol. Chem. 35 (1960) 94–131.
[3] S. Piccarolo, Phys. J. Macromol. Sci. B31 (1992) 501–511.
[4] V. Brucato, G. Crippa, S. Piccarolo, G. Titomanlio, Polym. Eng. Sci. 31 (1991) 1411–1416.
[5] V. Brucato, S. Piccarolo, V. La Carruba, Chem. Eng. Sci. 57 (2002) 4129–4143.
[6] C.C. Hsu, P.H. Geil, H. Miyaji, K. Asai, J. Polym. Sci., Polym. Phys. 24 (1986) 2379–2401.
[7] V. Caldas, G.R. Brown, R.S. Nohr, J.G. MacDonald, L.E. Raboin, Polymer 35 (1994) 899–907.
[8] Y. Miyamoto, K. Fukao, T. Yoshida, N. Tsurutani, H. Miyaji, J. Phys. Soc. Jpn. 69 (2000) 1735–1740.
[9] S.A. Adamovsky, A.A. Minakov, C. Schick, Thermochim. Acta 403 (2003) 55–63.
[10] M. Merzlyakov, Thermochim. Acta 403 (2003) 65–81.
[11] S. Adamovsky, C. Schick, Thermochim. Acta 415 (2004) 1–7.
[12] A. Gradys, P. Sajkiewicz, A.A. Minakov, S. Adamovsky, C. Schick, T. Hashimoto, K. Saijo, Mater. Sci. Eng. A413–414 (2005) 442–446.
[13] F. De Santis, S. Adamovsky, G. Titomanlio, C. Schick, Macromolecules 39 (2006) 2562–2567.
[14] C. Silvestre, S. Cimmino, D. Duraccio, C. Schick, Macromol. Rapid. Commun. 28 (2007) 875–881.
[15] F. De Santis, S. Adamovsky, G. Titomanlio, C. Schick, Macromolecules 40 (2007) 9026–9031.
[16] Q. Zia, R. Androsch, H.-J. Radusch, S. Piccarolo, Polymer 47 (2006) 8163–8172.
[17] Q. Zia, H.-J. Radusch, R. Androsch, Polymer 48 (2007) 3504–3511.
[18] R. Androsch, Macromolecules 41 (2008) 533–535.
[19] Q. Zia, D. Mileva, R. Androsch, Macromolecules 41 (2008) 8095–8102.
[20] D. Mileva, R. Androsch, H.-J. Radusch, Polym. Bull. 61 (2008) 643–654.
[21] D. Mileva, R. Androsch, H.-J. Radusch, Polym. Bull. 62 (2009) 561–571.
[22] H.J. Zimmermann, J. Macromol. Sci., Phys. B32 (1993) 141–161.
[23] K. Jeon, Y.L. Chiar, R.G. Alamo, Macromolecules 41 (2008) 95–108.
[24] C. De Rosa, F. Auriemma, O. Ruiz de Ballesteros, L. Resconi, I. Camurati, Macromolecules 40 (2007) 6600–6616.
[25] P.C. Poon, P. Dias, P. Ansems, S.P. Chum, A. Hiltner, E. Baer, J. Appl. Polym. Sci. 104 (2007) 489–499.
[26] C. Marega, A. Marigo, R. Saini, P. Ferrari, Polym. Int. 50 (2001) 442–448.
[27] T. Foresta, S. Piccarolo, Goldbeck-Wood, Polymer 42 (2001) 1167–1176.
[28] C. Silvestre, S. Cimmino, R. Triolo, J. Polym. Sci., Polym. Phys. 41 (2003) 493–500.
[29] Private communication, Borealis, Linz, January 2009.
[30] A.A. Minakov, C. Schick, Rev. Sci. Instrum. 78 (2007) 1–10.
[31] Y.L. Gao, E. Zhuravlev, C.D. Zou, B. Yang, Q.J. Zhai, C. Schick, Thermochim. Acta 482 (2008) 1–7.
[32] B. Wunderlich, Pure Appl. Chem. 67 (1995) 1019, Internet: http://athas.prz.rzeszow.pl, M. Pyda (Ed.).

[33] I.S. Kolesov, R. Androsch, H.-J. Radusch, J. Therm. Anal. Calorim. 78 (2004) 885–895.
[34] P.J. Flory, J. Chem. Phys. 17 (1949) 223–240.
[35] I.C. Sanchez, R.K. Eby, Macromolecules 8 (1975) 638–641.
[36] R.G. Alamo, A. Gosal, J. Chatterjee, K.L. Thompson, Polymer 46 (2005) 8774–8789.
[37] K. Jeon, H. Palza, R. Quijaba, R.G. Alamo, Polymer 50 (2009) 832–844.
[38] A.A. Minakov, D.A. Mordvintsev, C. Schick, Polymer 45 (2004) 3755–3763.
[39] A.A. Minakov, D.A. Mordvintsev, C. Schick, Faraday Discuss. 128 (2005) 261–270.
[40] A.A. Minakov, D.A. Mordvintsev, R. Tol, C. Schick, Thermochim. Acta 442 (2006) 25–30.
[41] R.T. Tol, A.A. Minakov, S.A. Adamovski, V.B.F. Mathot, C. Schick, Polymer 47 (2006) 2172–2178.
[42] B. Wunderlich, Crystal Nucleation, Growth, Annealing Macromolecular Physics vol. 2, Academic Press, New York, 1976.
[43] G. Strobl, The Physics of Polymers, Springer, Berlin, 2007.
[44] A. Fichera, R. Zannetti, Makromol. Chem. 176 (1975) 1885–1892.
[45] R. Zannetti, G. Celotti, A. Fichera, R. Francesconi, Makromol. Chem. 128 (1969) 137–142.
[46] A. Minakov, A. Wurm, C. Schick, Eur. Phys. J. Soft Matter 23 (1) (2007) 43–53.